

A New Acceptor (N-type) Polyphenylenevinylene Building Block: SF-PPV-I

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Abstract

A new sulfone derivatized acceptor (n-type) polyphenylenevinylene “SF-PPV” with nano meter sizes and functional terminals has been synthesized and characterized. The SF-PPV-I that contains hydrocarbon alkyl-sulfone moieties has a strong photoluminescence in both solution and in solid thin film states. In dichloromethane, the 5-10 nm sized SF-PPV has a maximum emission at about 530 nm with excitation maximum at about 490 nm. UV-VIS shows a absorption peak onsite at about 500 nm. Optical spectroscopy and electrochemical studies revealed that the SF-PPV-I has an LUMO level at about –3.6 eV (relative to vacuum), and an HOMO level at about –6.1 eV. The average size (length) of SF-PPV-I can be controlled on the nano meter scale via synthetic means. The SF-PPV has the potential in developing polymer based supramolecular opto-electronic semiconductor devices.

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Conjugated electro-active polymers find their potential applications in many future electronic and photonic devices, particularly in inexpensive and flexible shaped opto-electronic (such as photovoltaic) or electro-optic (such as electroluminescent) devices.¹⁻² In many of these materials systems, variety donor (p-type) and acceptor (n-type) moieties are needed in order to fabricate and fine-tune the electronic and other properties of the desired materials and structures. While many donor type of conjugated polymers, such as Polyanilines, donor substituted Polyphenylenevinylenes (PPVs) or Polythiophenes, etc.,¹ have been widely studied and developed in past several decades, there are relatively fewer acceptor type of conjugated polymers being developed. A few important acceptor type conjugated organic systems already developed include, *e.g.*, C₆₀, CN-PPV, BBL, etc.¹⁻² Due to certain disadvantages of these systems, such as poor processability or functionalization limitations, and the complexity of future electronic or photonic device needs, better and synthetically amenable new acceptor type conjugated polymers need to be developed.²⁻³ We have earlier presented a sulfone-2-ethyl-hexyl derivatized PPV based on Wittig-HWE type coupling.^{3d} Recently, we noticed that a variant non functional sulfone-alkyl derivatized PPV based on Heck type coupling was reported but without details.^{3g} In this paper, we describe the synthesis and report key optical and electronic properties of the terminally functional sulfone-alkyl derivatized polyphenylenevinylene or

SF-PPV-I. SF-PPV-II refers to the functional fluorinated SF-PPV analogs that we will report separately.

Scheme 1 shows the synthesis of **6** (SF-PPV-I) with either di-aldehyde or di-phosphate ended functional PPV blocks. Similar synthetic approaches have been used in synthesizing alkyloxy derivatized donor type PPV oligomers and polymers before.⁴ One advantage of this synthetic scheme is that the synthesized **6** is functional at both ends, and therefore can be further reacted to form block copolymer supramolecular structure.^{3a-e} In our scheme, 4-mercaptophenol **1** was derivatized first (via Williamson ether coupling) with RO and SR side chains (In our experiments, R is an alkyl units with 2, 8 and 10 carbons) in order to investigate reactivity, processability and other properties of the materials. Compound **3** was synthesized using a modified dibromomethylation reaction.⁵ In this step, compounds with C₂H₅ chains appear having the best reactivity, best yield, and easiest purification, yet the solubility of final PPV blocks were not as good as the C₈H₁₇ or C₁₀H₂₁ derivatized ones. For instance, the dibromomethylation reaction of **2** with C₂H₅ substituted ones typically completed in two days, that was in contrast to at least a week for the C₈H₁₇ or C₁₀H₂₁ ones. This is possibly due to that the bulky groups of the C₈H₁₇ or C₁₀H₂₁ may hinder the dibromomethylation reaction sites nearby the RO or SR chains. For the C₂H₅ substituted compounds, the mono-substituted product is in liquid form and is soluble in formic acid, while the di-substituted product precipitates out of solution as a white solid. The product can be purified conveniently from recrystallization in methanol. For C₈H₁₇ or C₁₀H₂₁ compounds, chromatography combined with recrystallizations are necessary to purify the product. For the synthesis of **4**, a neat reaction in triphosphite was used. If a solvent is present, the reaction cannot be completed even after 72 hours. A short air-cooled condenser was employed so that the by-product, bromo-ethane can escape from the system. In the last step of monomer **5** synthesis, hydrogen peroxide was used to

oxidize the sulfide into sulfone in acetic acid.⁶ All synthesized compounds were characterized by NMR, high resolution mass, etc. The SF-PPV-I block **6** was synthesized via the Wittig-HWE type coupling⁷ between monomer **5** and benzene dialdehyde. For dialdehyde terminated **6**, ¹H NMR indicated the disappearance of phosphate groups and the appearance of alkene protons (6.8-7.0 ppm) after PPV was formed. Appearance of strong luminescence is another indication of PPV formation. Both the terminal functional groups and the average size of SF-PPV-I can be controlled by the monomer ratio, reaction time, reaction temperature, etc. Table 1 list octyl substituted and dialdehyde terminated **6** with different lengths. Size control is very critical in building nano structured supramolecular systems.³

The photo luminescence spectra of SF-PPV-I (both excitation and emission) in methylene chloride were shown in figure 1. In excitation scan, the detector is set at 530 nm (the emission maximum). In emission scan, the excitation is set at 490 nm (the excitation maximum). Figure 2 is the UV-Vis of **6** that shows an onset absorption at about 500 nm. The Cyclic Voltammetry (CV) scan of **6** is shown in figure 3. A cathodic peak starts at about -0.7 volt. From experimental optical and electrochemical data, and based on a widely used model,⁸ we estimated the LUMO level (relative to vacuum) of SF-PPV-I is about -3.6 eV, and HOMO level is about -6.1 eV.

In summary, a new processable, terminally functionalized acceptor (n-type) sulfone alkyl derivatized conjugated polyphynylenevinylene “SF-PPV-I” has been synthesized and characterized. Since the sulfone group is a well-known strong electron-withdrawing group, the SF-PPV-I is expected to be a good acceptor (n-Type) conjugated polymer. More importantly, the functional terminals of SF-PPV-I offer convenience for synthesizing block copolymer nano structures. The average size of SF-PPV-I can be controlled via synthetic conditions. Finally, the SF-PPV-I can be coupled with donor (p-type) conjugated polymers (such as RO-PPV) to fabricate P/N heterojunction related opto-electronic devices.

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Supporting Information Available

Synthesis and characterization details (including NMR, mp, HR-MASS data, etc.) of **1-6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. Block Size of SF-PPV-I vs. Synthetic Condition (Reaction condition: dry THF/NaH, room temperature, 24 hours)

ID	Monomer ratios (monomer 5:dialdehyde)	Average Mw (Via GPC)	Average Repeat Units	Average Size (nm)	PD
1	1:0.80	3,800	7	8	1.59
2	1:0.85	7,050	14	17	1.84
3	1:0.90	8,800	17	20	2.16

Scheme and Figure Captions

Scheme1. Synthetic Scheme of SF-PPV-I

Figure 1. PL excitation and emission spectra of SF-PPV-I (in CH₂Cl₂, Mw~2000, average repeat unit=6, or 7nm average size.)

Figure 2. UV-Vis absorption of SF-PPV-I

Figure 3. Cyclic Voltammogram of SF-PPV-I (in dry and purged DMF with 0.1M Bu₄NPF₆ as electrolyte, working electrode: Ag/AgCl, scan rate 100mV/s)

Scheme1

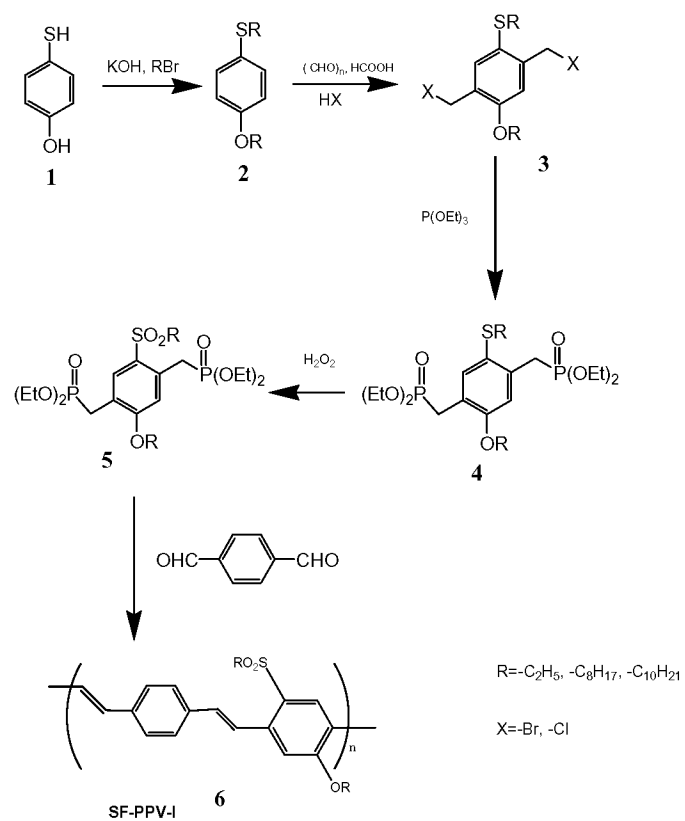


Figure 1

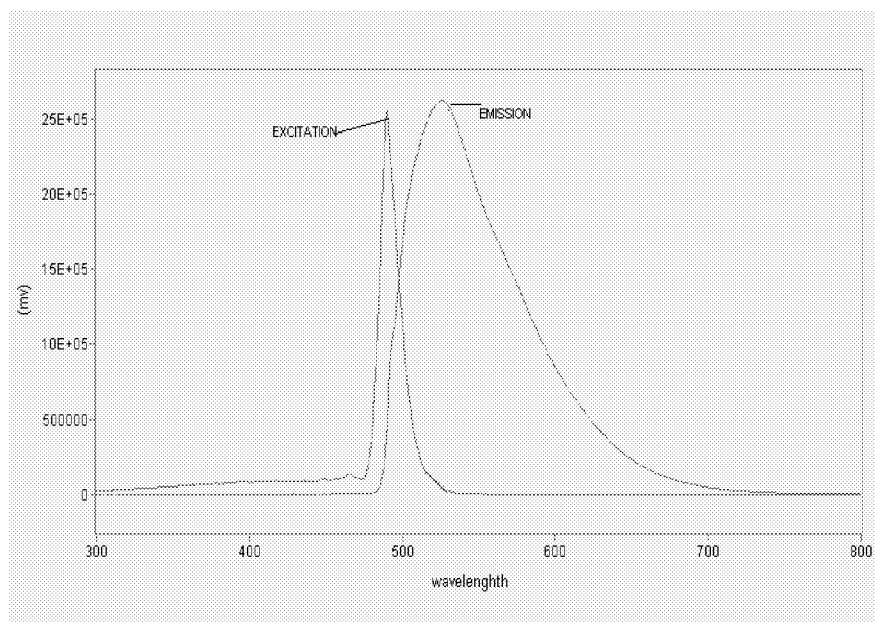


Figure 2

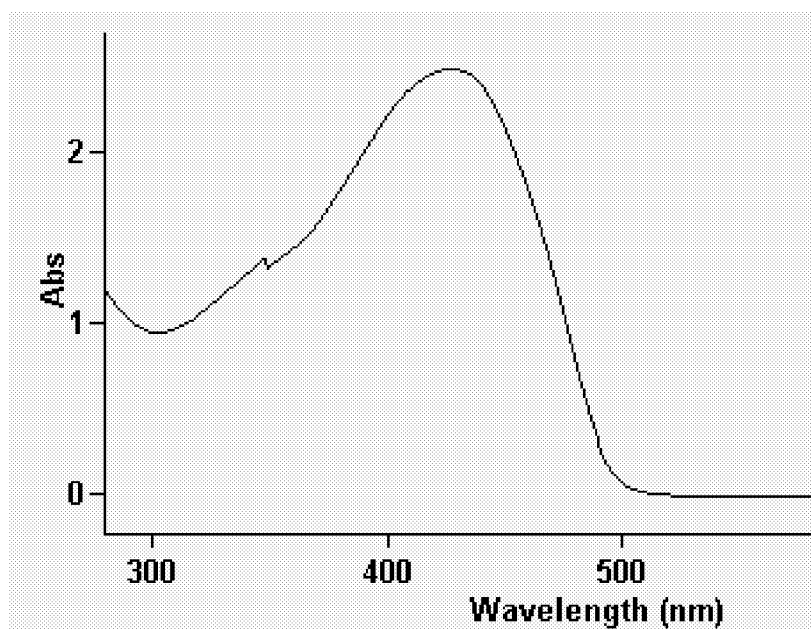


Figure 3

